REMOVAL OF MANGANESE FROM SYNTHETIC WASTEWATER BY ADSORTPION

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NOMENCLATURE

C_B	Bulk concentration of Mn^{2+} , kg/m^3
Co	Initial concentration of Mn^{2+} , mg/L
Ci/C_T	Relative concentration, mol/L
C_f	Final concentration of Mn^{2+} , mg/L
k_1	Equilibrium constant, min^{-1}
k_1	Lagergen pseudo-first order adsorption rate constant, min^{-1}
k_2	Second order adsorption rate constant, kg/kg.min
K	Langmuir equilibrium constant, m^3/kg
m	Dry weight of adsorbent, kg
m_a	Amount of adsorbent dosage, g
q	Amount adsorbed, kg/kg
q_e	Amount of heavy metal ion adsorbed at equilibrium, kg/kg
q_{max}	Maximum capacity adsorption, kg/kg
q_t	Amount adsorbed at time t, kg/kg
q_∞	Maximum adsorption capacity for Langmuir model, kg/kg
R	Percentage removal, %
R_L	Type of adsorption isotherm
t	Time, min
V	Volume of aqueous phase, m^3
w_a	Adsorbent dosage , kg

PENYINGKIRAN MANGAN DARI SINTETIK AIR MENGGUNAKAN PENJERAPAN

ABSTRAK

Logam berat dianggap sebagai pencemar dalam pelbagai industri dan merupakan masalah alam sekitar yang serius. Industri membebaskan jumlah logam berat yang banyak dan kepekatan tinggi ke dalam air. Apabila menggunakan air bawah tanah sebagai air minuman, penyingkiran mangan telah menjadi masalah terutamanya di bandar-bandar besar. Objektif penyelidikan ini adalah untuk mensintesis dan menentukan cirri-ciri MOCZ untuk penyingkiran Mn^{2+} dari sintetik sisa air dengan mengetahui hubungan masa yang dijalankan, kandungan MOCZ, pH, kepekatan Mn^{2+} yang berbeza terhadap kapasiti penjerapan. Keseimbangan data ditentukan dengan menggunakan Langmuir dan modified Langmuir model. Ciri-ciri MOCZ yang ditentukan termasuk keluasan permukaan MOCZ, isipadu liang, sifat morfologi dan komposisi mineralogy MOCZ dengan masing-masing menggunakan BET, FESEM dan XRD. Penjerapan eksperimen telah dijalankan dengan kepekatan Mn^{2+} yang berbeza dari 50mg/L hingga 200 mg/L pada kelajuan penggoncang 150 rpm selama 120 minit. Dari hasil yang diperolehi, MOCZ mempunyai darjah penghabluran yang rendah, dan oksida yang disalut pada permukaan zeolite adalah vernadite ($\delta MnO2$) dengan keluasan permukaan 39.9 m^2g^{-1} dan purata saiz diameter liang sebanyak 1.1733nm. Keputusan menunjukkan bahawa jumlah penjerah Mn^{2+} meningkat dengan pH dan kandungan MOCZ dan kajian kinetik penjerapan menunjukkan penjerapan Mn^{2+} mengikut model pseudo-tertib kedua. Tambahan pula, two sites one molecule bersesuaian dengan data, menunjukkan penjerapan yang kuat dengan kapisiti penjerapan Mn^{2+} sebanyak 0.9267 meq Mn^{2+} g^{-1}. Keputusan menunjukkan bahawa MOCZ berpotensi baik sebagai adsorben Mn^{2+} ion.

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ABSTRACT

Heavy metals are considered as pollutants in variety of industrial effluents and it is considered as a serious environmental problem. Industries release various concentration and amounts of heavy metals into water. However, when using groundwater as drinking water, manganese removal has become a problem especially in big cities. The objectives of this research was to synthesize and characterize of MOCZ for the removal of Mn^{2+} from synthetic wastewater by conducting the effect of contact time, adsorbent dosage, pH and initial Mn^{2+} concentration on adsorption capacity. The equilibrium data were fitted by using Langmuir and modified Langmuir isotherm model. Characterization of MOCZ were including specific surface area, pores volume, morphology properties and the mineralogical composition by using BET, FESEM and XRD respectively. Batch adsorption experiments were studied at different initial concentration from 50 mg/L to 200 mg/L at 150 rpm agitation speed for 120 min. The MOCZ showed low crystallinity degree, and the oxide coated on zeolite surface was presented mainly as vernadite (δMnO2) with specific surface area 39.9 m^2g^{-1} and average pore size diameter of 1.1733 nm. Results showed that the amount of Mn^{2+} adsorbed increased with pH and adsorbent dosage and that the adsorption kinetics study of the Mn^{2+} followed a pseudo-second-order model. Furthermore, the two sites one molecule mechanism fitted well equilibrium data, showing a strong adsorption capacity for Mn^{2+} ions reaching a maximum capacity of 0.9267 meq $Mn^{2+}g^{-1}$. Results found showed that MOCZ showed a good potential as adsorbent for Mn^{2+} ions.

CHAPTER 1

INTRODUCTION

1.1 Background of study

The demand of water has increased tremendously with agricultural, industrial and domestic sectors each consuming 70%, 22%, and 8% of the available fresh water and generate large amount of wastewater containing a number of pollutants (Helmer & Hespanhol, 1997). A government report by United Nations Environment Programme East Asian Regional Coordinating Unit, 1994 found that states such Penang, Perak, Selangor and Melaka consisted of highest concentrations of heavy metal in wastewater. However, almost all major rivers, mudflats and coast water near industrialized sites are polluted. This occurred because of poor sewage disposal systems, lack of treatment technologies and indiscriminate discharge of toxic materials from industries (Fu & Wang, 2010). Furthermore, wastewater treatment process need high capital expenditures as the establishment of the drainage system will cost billions of ringgit to the government. Besides that, it is not easy to purify and it may take years to remove the pollutant (Indah Water Konsortium, 2002).

Heavy metals are considered as pollutants in variety of industrial effluents. The increasing contamination of urban and industrial wastewater by toxic metal ions is a serious environmental problem (Mengistie, et al., 2012). Industries such as metal plating, metal finishing, rubber processing, mining, as well as chemical manufacturing release various concentration and amounts of heavy metals into the surface and ground water (Southichak, et al., 2006). These trace elements are considered as toxic and most of the contaminants are released into the environment in high amount that cause risk to human health (Tiller, 1989).

As far as is known, humans suffer no harmful effects from drinking water containing manganese. However, when using groundwater as drinking water, manganese removal has become a problem especially in big cities (Taffarel & Rubio, 2010). According to the Malaysia Sewage & Industrial Effluent Discharge Standard (2000), the discharge limit for manganese in industries is 0.2 mg/L for standard A and 1 mg/L for standard B. Processing industries such as Lynas and other industries discharge amount of manganese into the river. However, manganese is not easily removed due to its high concentration. Manganese interferes with laundering operation, impacts objectionable stains to plumbing fixture, and causes trouble in distribution systems by supporting growth of iron bacteria (Mengistie, et al., 2012). For human cases, the bad effects of long exposure to manganese may affect the central nervous system as well as lung tissue (Fu & Wang, 2010).

In order to remove heavy metals effectively from wastewater, various process for the treatment have been developed, such as chemical precipitation, ion-exchange, membrane separation and adsorption (Mohan & Singh, 2002). Conventional treatment for manganese removal generally required the use of strong oxidizing agents such as potassium permanganate, chlorine, hypochlorite, chlorine dioxide or ozone (Teng et al., 2001). Therefore, reactive process (adsorption) should be used for heavy metal removal where the adsorbent used should have chemical reactivity towards heavy metals.

1.2 Problem Statement

Nowadays, the increased disposal of heavy metals in water is due to rapid growth and developments of industries. Industries such as electroplating, metallurgical process, mining, chemical manufacturing industries release various concentrations of heavy metals. Metal ions such as cadmium, chromium, copper, lead, zinc, manganese and iron are commonly detected in both natural and industrial effluents (Sayed et al., 2011). In recent years, this problem has received attention as heavy metals in water can be absorbed by marine and human bodies which cause health risk. At high concentration, heavy metals can considerable effects on the health of living organisms such as carcinogens and mutagens (Fu & Wang, 2010).

A number of technologies can be used in order to remove heavy metals from the contaminated wastewater such as filtration, adsorption, chemical precipitation, ion exchange and membrane separation. However, most of this method might not be efficiency in removing heavy metal at very low concentrations, and could be relatively expensive (Mengistie, et al., 2012). These methods are also not effective due to their secondary effluent impact on the recipient environment (Sharma &

Forster, 1994). For this reason, the uses of low-cost materials for adsorbent of metals from contaminated wastewater have been popular.

Adsorption process provides an attractive and alternative treatment compared to other removal techniques because it is more economical and readily available. Zeolite is one of the common adsorbents used in adsorption process. Zeolites have been used as adsorbents, molecular sieves, membranes, ion-exchangers and catalyst, mainly because zeolite exchangeable ions are relatively innocuous (Taffarel & Rubio, 2008). Thus, zeolites are particularly suitable for removing undesirable heavy metal ions wastewater. In order to improve the adsorption capacity and mechanical strength of zeolite, severals methods have been used to modify natural zeolites by either physical or chemical reactions. Therefore, synthesizing of the adsorbent is a challenge to produce an alternative and effective adsorbent.

1.3 Objectives

The objectives of this research are:

i. To synthesize and characterize of MOCZ for the removal of Mn^{2+} from synthetic wastewater

ii. To study the effect of contact time, adsorbent dosage, pH and initial Mn^{2+} concentration on adsorption capacity

iii. To determine the best correlation to the equilibrium data using Langmuir and modified Langmuir isotherm model

1.4 Scope of research

The scopes of this research are:

i. The effect of contact time on the adsorption capacity which is used to find the equilibrium time

ii. The effect of initial concentration of Mn^{2+} aqueous solution which is 50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L

iii. The effect of pH of Mn^{2+} aqueous solution change where the pH is adjusted at 4, 5, 6, 7 and 8

iv. Characterization of MOCZ in terms of specific surface area, pores volume, morphology properties and mineralogical composition

1.5 Significance of study

The rationales of significances of this study are:

i. To prevent the heavy metal concentration release to the water stream which can cause toxicity that can be potential hazard to human health and environment

ii. To reduce the cost of wastewater treatment by using modified zeolite due to its high abundance and high affinity for metal ions

iii. To improve the current adsorption process in wastewater treatment by using modified zeolite

CHAPTER 2

LITERATURE REVIEW

2.1 Wastewater

Wastewater is any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharged by domestic residences, commercial properties, industry and agriculture and can encompass a wide range of potential contaminants and concentrations (Salam et al., 2011). The domestic water used for normal activity in homes, businesses and institutions (Helmer & Hespanhol, 1997). The domestic wastewater is readily treatable industrial. The characteristics of industrial wastewater depends on the type of industry using the water .Some industrial wastewaters can be treated the same as domestic wastes without difficulty.

There's may contain toxic substances or high percentages of organic materials or solids which make treatment difficult. In such cases, the industrial plant may have to pretreatment its wastewater to remove these pollutants or reduce them to treatable levels before they are accepted into a general treatment facility. In most common usage, it refers to the municipal wastewater that contains a broad of spectrum of contaminants resulting from the mixing of wastewaters from different sources.

Wastewater is one of the most serious environmental problems. The major source of water pollution in the country is domestic wastewater discharge. The need for the provision of wastewater collection and treatment facilities has long been identified by government as a part of its efforts to protect the environment and well being of the population. However, when these facilities were handed over to local government authorities to operate and maintain, the concerned government agency had difficulty to manage the facilities in a sustainable manner due to inadequate planning, budgeting and ownership (Indah Water Konsortium, 2002).

According to Malaysia's Environmental Law, Environmental quality act, 1974, Malaysia Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, 1999, 2000,

Table 2.1 Parameter limits of effluent of standard A and B

Parameter	Standard A	Standard B
Temperature (^oC)	40	40
pH value	6.0-9.0	5.5-9.0
BOD5 at 20^oC	20	50
	Heavy metal (mg/L)	
Mercury	50	0.05
Cadmium	50	0.02
Chromium, Hexavalent	0.005	0.05
Arsenic	0.01	0.10
Cyanide	0.05	0.10
Lead	0.10	0.5
Chromium, Trivalent	0.20	1.0
Copper	0.20	1.0
Manganese	0.20	1.0
Nickel	0.20	1.0
Tin	0.20	1.0
Zinc	1.0	1.0
Boron	1.0	4.0
	Other pollutants (mg/L)	
Iron (Fe)	1.0	5.0
Phenol	0.001	1.0
Free Chlorine	1.0	2.0
Sulphide	0.5	0.5
Oil and Grease	Not detectable	10.0

2.1.1 Characteristic of Wastewater

Wastewater can be categorized into two characteristics, which is the physical and chemical characteristic.

2.1.1.1 Physical Characteristic

Characteristics of wastewater are detected through the physical senses: temperature, odor and color. Fresh wastewater is turbid, grayish-white in color and has a musty odor. Small particles of feces and paper are visible in the waste stream, but these will rapidly settle if the wastewater is quiescent. Table 2.2 shows the significant colors of wastewater.

Table 2.2: Significant colors in wastewater (Win, 2003)

Color	Problem indicated
Gray	None
Green, yellow or other	Industrial wastes not pretreated
Red	Blood, other industrial wastes or TNT complex
Red or other soil color	Surface runoff into influent, also industrial flows
Dark brown to black	Hydrogen sulfide
Black	Septic conditions or industrial flows

2.1.1.2 Chemical Characteristic

Wastewater is composed of organic and inorganic compounds as well as various gases. Organic components may consist of carbohydrates, proteins, fats and greases, surfactants, oils, pesticides and phenol. Inorganic components may consist of heavy metals, nitrogen, phosphorus, pH, sulfur, chlorides, alkalinity and toxic compounds (Peavy et al., 1985).

2.2 Treatment for heavy metal removal

There are several methods which have been used for the removal of heavy metals from wastewater such as chemical precipitation, ion exchange, membrane separation and adsorption (Mohan & Singh, 2002).

2.2.1 Chemical Precipitation

Chemical precipitation is the most effective method on removing heavy metal from wastewater. According to Fu & Wang (2011), chemical precipitation method is simple and inexpensive to operate. During precipitation process, the chemical will react with heavy metal ions to form insoluble solid. Then, the precipitates formed can be separated by filtration. However, this method will produce large amount of sludge which can lead to the disposal problem (Iwa Water Wiki, 2010). Ceribasi & Yetis (2010) also mentioned that concentration limits are one of the problems which may cause chemical precipitation process become expensive and ineffective in wastewater treatment. Chemical precipitation will cause serious disposal problem which produce large amount of sludge to be treated. Grandt & Mcdonald (1981) proved that chemical precipitation is not suitable to be used because this method have a major disadvantage to the requirement of large doses of alkaline materials to increase and maintain pH values typically from 4.0 to 6.5 for optimal metal removal.

2.2.2 Ion Exchange

Ion-exchange processes have been widely used to remove heavy metals from wastewater due to their advantages, such as high treatment capacity, high removal efficiency and fast kinetics (Kang et al., 2004). Ion-exchange resin, either synthetic or natural solid resin, has the specific ability to exchange its cations with the metals in the wastewater. Among the materials used in ion-exchange processes, synthetic resins are commonly preferred as they are effective to nearly remove the heavy metals from the solution (Alyuz & Veli, 2009). The most common cation exchangers are strongly acidic resins with sulfonic acid groups ($–SO_3H$) and weakly acid resins with carboxylic acid groups (–COOH). Hydrogen ions in the sulfonic group or carboxylic group of the resin can serve as exchangeable ions with metal cations. The uptake of heavy metal ions by ion-exchange resins is rather affected by certain variables such as pH, temperature, initial metal concentration and contact time (Altun and Pehlivan, 2006). Ionic charge also plays an important role in ion-exchange process.

2.2.3 Membrane Separation

Membrane filtration is a thin layer of material capable of separating substances when a driving force is applied across the membrane. Membrane filtration showed high efficiency of removal of heavy metal, easy operation and also space saving (Fu & Wang, 2011). It also produced less solid waste and chemical consumption. However, Fu & Wang (2011) also found that this method is not suitable to removal heavy metal since it is high cost, complexity process and it will cause membrane fouling. These statements are supported by Chang & Kim (2005) that membrane filtration will cause the membrane fouling which leads to a frequent cleaning and replacement of membranes and will increase the operating cost. Therefore, the removal efficiency of single metal will decrease since there is present of other metals.

2.2.4 Adsorption

Adsorption process is widely used in wastewater treatment. In adsorption process, one or more components of gas and liquid stream are adsorbed on the surface of a solid adsorbent and a separation is accomplished (Geankoplis, 2008). Application of adsorption process include removal of organic compounds from water, coloured impurities from organics, fructose from glucose using zeolite and fermentation products from fermentor effluents. There are various types of low cost adsorbents which are derived from agricultural waste, industrial by product, natural material, or modified biopolymers (Barakat, 2010). These adsorbents are applied for the removal of heavy metals from metal-contaminated wastewater.

2.3 Adsorbent

There are several types of adsorbents used in adsorption process such as activated alumina, silica gel, activated carbon, molecular sieve carbon, molecular sieve zeolites and polymeric adsorbent (Geankoplis, 2008).

Activated alumina is a synthetic porous crystalline gel, which is available in the form of granules of different sizes having surface area ranging from 200 to 300 m^2g^{-1} (Gupta & Suhas, 2009). Bauxite a naturally occurring porous crystalline alumina contaminated with kaolinite and iron oxide normally having surface area ranging from 25 to 250 m^2g^{-1}. According Geankoplis (2008), hydrated aluminium oxide is activated by heating to drive off the water. It is mainly used to dry gases and liquids.

Activated carbon is the most common adsorbent used and it is usually prepared from coal, coconut shells, lignite and wood. Normally, activated carbon has a very porous structure with a large surface area ranging from 500 to 2000 m^2g^{-1} (Gupta & Suhas, 2009). Studies have shown that activated carbons are good adsorbents for the removal of different types of adsorption process but the used of the adsorbent is restricted due to their highest cost (Fu & Wang, 2011). Also, the activated carbons after their use in wastewater treatment become exhausted and are no longer capable of further adsorbing process. It has to be regenerated for further use in purifying water. Furthermore, the regeneration process will result in a loss of carbon and the regenerated product may have a slightly lower adsorption capacity in comparison with virgin activated carbon. However, Monser & Adhoum (2001) showed in their studies that modified activated carbon enhance the removal capacity for the inorganic pollutants.

Silica gel is incompletely dehydrated polymeric structure of colloidal silicic acid with formula $SiO_2.nH_20$ (Ng et al., 2001). It is prepared by the coagulation of colloidal silicic acid results in the formation of porous and nancrystalline granules of